A NEW TYPE OF REDUCTOR AND ITS APPLICATION TO THE DETERMINATION OF IRON AND OF VANADIUM.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science in
Columbia University.

BY

JAMES M. HENDEL, Litt.B.

NEW YORK CITY

1922

A NEW TYPE OF REDUCTOR AND ITS APPLICATION TO THE DETERMINATION OF IRON AND OF VANADIUM.

———

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science in
Columbia University.

———
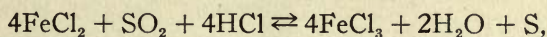
BY

JAMES M. HENDEL, Litt.B.

NEW YORK CITY

1922

DEDICATED TO MY FATHER

It gives the author much pleasure to acknowledge his indebtedness to Professor H. T. Beans for his open-minded, scientific attitude, for his stimulating criticism, and for his valued advice given throughout the course of this work.

In any analysis where an oxidimetric titration is employed, it is essential that the reducing agent be one which is oxidized to a chemical entity not affected by the titrating fluid, and that the excess of the reducing agent be completely and easily removable. These conditions are not entirely fulfilled by some of the more common reducing agents. It is well known that hydrogen sulfide, in reducing, is converted into substances of undefined composition titrable by permanganate solution; and that long-continued boiling in a stream of carbon dioxide is necessary to ensure complete removal of the excess hydrogen sulfide. A recent article published by Lundell and Knowles[1] gives a more complete account of the errors and difficulties involved in the use of hydrogen sulfide. Sulfur dioxide solutions and alkali sulfites, unless freshly prepared, usually contain other oxidizable substances not removable by boiling.[2] The reduction with sulfur dioxide requires a chloride solution for rapid reaction, which necessitates either the use of "preventive solution," as in the Zimmermann-Reinhardt method for iron, or the use of dichromate with an external indicator, neither of which methods is comparable in precision with a permanganate titration in sulfate solution. The use of this gas in the reduction of iron solutions is further complicated by the fact, shown by Wardlaw and Clews,[3] that ferrous chloride, in the presence of hydrochloric acid, is oxidized by sulfur dioxide in accordance with the equation:

$$4FeCl_2 + SO_2 + 4HCl \rightleftarrows 4FeCl_3 + 2H_2O + S,$$

the reaction producing a maximum of ferric ion of about 9 per cent. The possibility of the sulfur thus formed being converted into polythionates by excess sulfur dioxide casts further doubt on the advisability of using this gas. Finally, with this gas, as with hydrogen sulfide, boiling in a current of carbon dioxide is required to expel the excess, which process requires considerable time.

From the viewpoint of the conditions above stated, hydrogen suggests itself as the reducing agent *par excellence*. It is oxidized to a definite entity, hydrogen ion, which is not titrable by permanganate. It can be easily and completely re-

moved; in fact its slight solubility at room temperature precludes the need for its removal. Moreover the reaction between permanganate and hydrogen, in the absence of a catalyst, is too slow to affect the end point in a permanganate titration.

To use hydrogen effectively as a reducing agent, a catalyst is necessary. It has been found that ferric sulfate solutions can be reduced quantitatively merely by bubbling the gas into the solution in which is immersed a platinized platinum gauze. It is not necessary to bubble the gas over the gauze; it is only necessary to saturate the solution with hydrogen and then to bring the solution into contact with the gauze; bubbling the gas into the solution serves to accomplish both these objectives. To make the process more efficient, a reductor has been devised on the baffle-plate principle, as shown in Figure
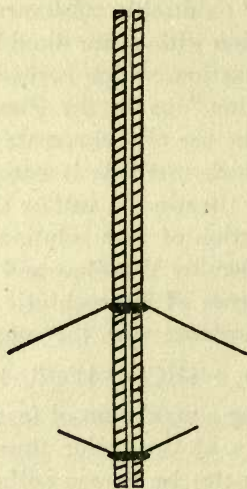

Fig. 1

I. It consists essentially of a capillary tube (bore 1 mm.) which passes through the center of two pieces of platinized platinum gauze which are held in place by small supports of glass fused to the glass capillary. The dimensions and relative positions of the two gauzes are determined largely by convenience, volume of solution, size of flask, etc., always keeping

8

in mind the fact that the speed of reduction increases with increase in the total surface of catalyst. One reductor was made with a lower gauze 2.25 × 2.50 cm. attached 0.5 cm. from the end of the capillary, with an upper gauze 3.5 × 4 cm. attached 3 cm. above the lower gauze and bent so as to imprison the gas bubbles leaving the lower gauze; at the upper gauze the small bubbles coalesce to a single large bubble which, on escaping, tilts the gauze and stirs the solution very effectively. Another reductor was made with three gauzes, of about the same total surface as the above, arranged, each with an upward tilt, so that every bubble came in contact with each gauze. No difference in speed of reduction was apparent.

The gauzes were plated with platinum black by electrolysis of chorplatinic acid at 3 volts and 0.6 amperes, then electrolyzed in dilute sulfuric acid for an hour to clean the gauze and to saturate it with hydrogen. For a total surface of 32 sq. cm., a deposit of from 0.1 to 0.3 grams of platinum was found to be sufficient. The activity of all reductors was found to increase with use. Three different reductors were used for about 100 determinations each, with an average reduction period of 1.5 hours, and have as yet shown no signs of decreased activity. When palladium black was used, the speed of reduction was increased, but no other effect was noticeable. For most purposes, platinum black should be effective enough. The reductors, when not in use, should be kept in distilled water, and in general, given the same careful treatment as an hydrogen electrode, to prevent "poisoning."

The object of this work is to apply the hydrogen reduction process to the determination of iron in ores and rocks. Since titanium and vanadium are usually associated with iron in these natural products, the effect of the reductor on both these elements must also be ascertained. The effect of the reductor on vanadium having been found, it was decided to apply the method to the determination of vanadium in steels.

Preparation of Materials.

Ferric alum (Kahlbaum's) was recrystallized twice. A solution of it was made up containing 10 g. of iron per liter with 20 c.c. of 18 M sulfuric acid per liter added to prevent

hydrolysis. The iron value was determined by careful reduction with a zinc reductor and titration with standard permanganate.

Titanium dioxide (Kahlbaum's) was dissolved in excess hydrofluoric acid, a solution of potassium-hydrogen-fluoride added, the crystals of potassium titanifluoride collected and recrystallized from hydrofluoric acid solution.[4] A solution containing 1.6 g. of titanium per liter was made up by weighing out the requisite amount of pure dry (110°) salt, treating with sulfuric acid in a platinum dish, fuming to get rid of all fluoride, then diluting with the required amount of water to make 1M sulfuric acid. The titanium content was checked by carefully evaporating a known volume of solution.

Ammonium vanadate (Merck's) was recrystallized, dissolved in hot water, made just acid to litmus with sulfuric acid, cooled and filtered. The resulting solution of vanadic acid was standardized by evaporating known volumes, igniting and weighing the residue as vanadium pentoxide. It contained 0.46 g. of vanadium per liter.

Potassium dichromate was recrystallized, then dissolved in acidified (sulfuric acid) water to make a solution containing about 15 g. of chromium per liter. As needed, portions of this solution were diluted to produce solutions of a more convenient concentration. The chromium content was determined by ferrous sulfate-permanganate titrations.

Permanganate solutions were usually about 0.013 Molar and 0.003 Molar (for vanadium titrations), standardized with Bureau of Standards sodium oxalate. The standard ferrous sulfate solution contained 30 g. of ferrous sulfate heptahydrate and 50 c.c. of concentrated sulfuric acid per liter.

The hydrogen used was taken from a tank, purified by passing it successively through neutral permanganate solution, cotton wool ,distilled water, and finally cotton wool; it was then led through black rubber tubing directly to the glass capillary of the reductor. Before using, each day, the "dead space" in the gas train was flushed out with a stream of hydrogen for from 10 to 15 minutes.

10

The Determination of Iron

Solutions containing 0.1 g. iron as ferric sulfate in volumes of from 100 to 150 c.c. have been reduced quantitatively under a variety of conditions. Whether the solution be hot or cold, strongly or weakly acid, complete reduction can be obtained if it be maintained for a long enough period. The time required has been found to depend chiefly on the size of reductor, rate of bubbling, temperature, and hydrogen ion concentration. No attempt has been made to determine the minimum dimensions of the reductor; a gauze 32 sq. cm. in size usually reduces 0.1 g. of iron in one hour, a gauze 62 sq. cm. in size requiring only three-quarters of an hour. The rate of bubbling has usually been regulated so as to stir the solution thoroughly; the reduction period could undoubtedly be decreased by more rapid bubbling, without danger either of losing the solution or of wasting the gas. Increase in temperature, except in weakly acid solutions where it promoted hydrolysis, decreased the reduction time. The usual procedure (designated as "hot, cool" in Table I) has been to start the heating at the same time as the reduction, continuing both processes until the hot solution showed no color of ferric ion, then cooling, either naturally, or more rapidly by immersing the flask in cold water, still maintaining the reduction, until room temperature was reached. Solutions colorless at 20° and apparently containing no ferric ion have occasionally shown incomplete reduction; solutions, colorless while hot, have always shown complete reduction; therefore to ensure complete reduction ,the solutions have been reduced until colorless at 80°–90° then cooled to 20° for titration. The time required for reduction was found to increase with the acidity. Solutions just acid to litmus and similar solutions containing in addition 3 c.c. of phosphoric acid (85 per cent.) in volumes of 100 to 150 c.c. have been reduced at 20° in one hour. Even solutions in 3 Molar sulfuric acid have been completely reduced, with or without heating, in one hour. But as a rule, an acidity greater than 0.5 M sulfuric acid increased the reduction period to more than one hour. In the absence of conditions requiring a higher acidity, the concentration of sulfuric acid for the reduction should be 0.5 Molar or less.

11

TABLE I.

No.	H_2SO_4 Molar	Temp.	Time Min.	Zn. R. c.c.	H. R. c.c.	Diff. c.c.
18	.05	20°	60	22.79	22.84	+.05
19	.10	20°	60	"	22.86	+.07
18a	.03	20°	70	"	22.75	—.04
19a	.1[1]	20°	80	"	22.80	+.01
33f	1.7	hot, cool[2]	60	34.22	34.26	+.04
33g	1.7	" "	140	"	34.23	+.01
44a	.5	" "	120	"	34.16	—.06
45	.5	" "	60	"	34.19	—.03
46	.5	" "	80	"	34.24	+.02
51	.7	" "	60	34.04	34.04	0
51a	.7	" "	60	"	"	0
52	.7	" "	160	"	"	0
52a	.7	" "	90	"	34.05	+.01
53	.7	" "	75	"	34.05	+.01
53a	.7	" "	80	"	34.06	+.02
54	.7	" "	90	"	34.05	+.01
54a	.7	" "	70	"	34.10	+.05
57	1.5[1]	" "	75	"	34.03	—.01
57a	1.4[1]	" "	90	"	34.03	—.01
58	1.5[1]	" "	80	"	33.97	—.07
58a	1.4[1]	" "	90	"	34.06	+.02

Note 1: Contains 3 c.c. 85% H_3PO_4 in addition to stated amount of H_2SO_4.

Note 2: Solutions were reduced hot till colorless, then cooled to 20° while reduction was maintained.

This table is representative of the results obtained with the above reduction process. The lettered numbers refer to the same solutions as the corresponding numbers unlettered. In every case, the same amount of iron (0.1 g.) was taken, the different titers resulting from the use of different permanganate solutions. The average difference between the two methods is less than one part per thousand.

Titanium

The effect of the hydrogen reductor on titanic sulfate solutions was studied. Previous investigators (Denham[5], Teletow[6], Diethelm[7], Eggert[8]) have found it impossible to completely reduce titanic ion to titanous ion by means of hydrogen and platinized platinum; the formation of titanous ion was

favored by increasing the hydrogen pressure and also by increasing the acidity, but increased temperature favored the formation of titanic ion. A maximum reduction of 61 per cent. was found by Eggert using a 0.21 N titanic sulfate solution, 2 N with respect to sulfuric acid, at 14°, although by electrolytic reduction, Diethelm secured 100 per cent. reduction of a 0.25 Molar titanic sulfate solution in an acid concentration of 0.657 Molar sulfuric acid and 99.9 per cent. reduction in a 0.560 Molar hydrochloric acid solution. The results listed in Table II show a maximum reduction of 71%. In experiments 2, 2a, 3, 3a, no attempt was made to prevent reoxidation by the air or by the oxygen dissolved in the water used for washing the reductor.

TABLE II.

Titanic Sulfate Solutions.

No.	H_2SO_4 Molar	Temp.	Time Min.	Vol. c.c.	Ti taken Grams	% Reduced
2	1.4	20°	60	130	.0999	70.93
2a	1.8	20°	60	100	.0999	71.20
3	.7	20°	150	130	.1004	70.82
3a	.5	20°	60	175	.1004	66.0
4	1.6	20°	120	130	.0400	27.1[1]
5	1.6	hot	120	130	.0400	19.7[1]
6	3.2	hot	90	130	.0800	29.5[1]

Note 1: Kept in atmosphere of H_2; boiled H_2O used for washing.

Solutions containing a fixed amount of ferric alum (0.1 g. of iron) and varying amounts of titanic sulfate were reduced under the various conditions stated in Table III. It may be observed from this table, that iron can be successfully determined in the presence of 0.0064 g. of Ti provided the acidity be less than 0.5 M sulfuric acid. For acidities equal to or greater than this, the presence of Ti in greater amounts than 0.0032 g. may cause high values for the iron content.

TABLE III.

10 c.c. Ferric Alum Solution with Varying Amounts of Ti.

No.	H_2SO_4 Molar	Temp.	Time Min.	Ti Grams	Zn. R. c.c.	H. R. c.c.
4b	.1	20°	60	.0016	22.79[1]	22.78
5c	.15	hot, cool	75	.0032	"	22.79
6c	.3	20°	60	.0048	"	22.74
7	.4	hot, cool	60	.0064	"	22.80
7a	.5	20°	60	.0064	"	23.17
8	.5	hot, cool	90	.0080	"	23.31
5d	1.0	20°	70	.0032	32.86[2]	32.82
4e	.8	hot, cool	75	.0032	"	32.91
6d	.3	hot, cool	75	.0048	"	32.81
7d	.3	20°	60	.0064	"	32.84
7b	.4	hot, cool	75	.0064	"	32.82
8b	.7	hot, cool	60	.0080	"	32.93
15	.1	20°	60	.0160	"	32.86
16	.1	20°	70	.0160	"	33.00[3]

Note 1: $KMnO_4$ Solution B, 1 c.c. = 0.00517 g. iron.
Note 2: $KMnO_4$ Solution C, 1 c.c. = 0.003585 g. iron.
Note 3: Reduced solution was colorless.

It is desirable, however, to extend the above limits, both as to acidity and to titanium content. With the latter object in view, ferric and titanic sulfate solutions were reduced after making the acid concentration 0.06 M sulfuric acid and boiling to precipitate titanium as titanium dioxide; in every experiment the iron value proved to be too low. It was then decided to take advantage of the extreme sensitivity of titanous ion and comparative stability of ferrous ion in acid solution toward atmospheric oxidation.[9] After reduction, oxygen from a tank, or purified air was bubbled into the cooled solution of ferrous and titanous ions without the reductor. Five or ten minutes of bubbling with a moderately fast current of air usually sufficed to reoxidize all titanous ion without affecting ferrous ion. By means of this expedient, 0.1 g. of iron was successfully determined in the presence of from 0.02 to 0.08 g. of titanium in solutions of acidity ranging from 0.1 to 3.0 M sulfuric acid. In all cases, the reduction was carried out at 20°, the violet color of titanous ion indicating when the iron was entirely reduced. Absence of this color did not warrant the conclusion that no titanic ion had been reduced, as may be seen from experiments 16d and 18a in Table IV.

14

TABLE IV.

Reduction of 10 c.c. Ferric Alum with Varying Amounts of Ti and Subsequent Reoxidation of Ti by Air or O_2.
Temperature $= 20°$, volume 100-150 c.c.

No.	Ti Grams	H_2SO_4 Molar	Time Min.	Time for Reoxidation	Theoretical Fe titer c.c.	Actual titer c.c.	Remarks
15b	.0160	.5	60	O_2 2 min.	32.86	32.80	
16b	"	.5	60	O_2 2 min.	"	32.90	
15c	"	1.0	70	O_2 2 min.	"	32.78	Faint violet
16c	"	1.0	60	none	"	32.89	Colorless
15d	"	1.5	75	O_2 3 min.	32.82	32.84	
16d	"	1.5	60	none	"	32.95	Colorless
15e	"	2.0	60	O_2 3 min.	"	32.80	Violet tinge
16e	"	2.0	60	O_2 3 min.	"	32.86	
6h	.0208	1.5	75	none	32.86	32.82	Colorless
6i	"	2.0	60	none	32.82	34.7	Reduced warm, violet tinge
7h	.0224	2.0	75	O_2 6 min	"	32.87	Colorless
7i	.0224	3.0	60	O_2 6 min.	"	32.76	
18	.0320	.15	60	O_2 2 min.	32.86	32.89	Violet tinge
19	"	.15	60	O_2 3 min.	"	32.86	" "
20	"	.15	60	none	"	32.86	
18a	"	.6	60	none	"	33.15	Colorless
19a	"	.6	90	O_2 6 min.	32.82	32.81	Violet tinge
20a	"	.6	75	O_2 3 min.	"	33.46	Violet tinge
18b	"	.6	60	O_2 6 min.	"	32.75	Colorless
19b	"	.6	60	O_2 6 min.	"	32.79	Violet
20b	"	.6	60	O_2 6 min.	"	32.88	Colorless
18c	"	1.0	75	Air 10 min.	"	32.79	Faint violet
19c	"	1.0	80	Air 15 min.	"	32.75	" "
20c	"	1.0	75	Air 5 min.	"	32.82	" "
18d	"	2.0	60	Air 10 min.	"	32.74	" "
19d	"	1.9	60	Air 5 min.	"	32.77	" "
18e	"	2.5	80	Air 5 min.	"	32.92	" "
19e	"	2.5	90	Air 10 min.	"	32.82	" "
20d	"	2.5	60	none	"	35.17	Violet
20e	"	3.0	60	Air 10 min.	"	32.83	"
21	.0798	.4	60	Air 5 min.	"	32.85	"
22	"	.4	60	Air 10 min.	"	32.86	"
21a	"	.9	60	Air 10 min.	"	32.76	Colorless
23	"	1.5	60	Air 10 min.	"	32.82	Faint violet
21b	"	2.0	60	Air 13 min.	"	32.80	" "
23a	"	2.5	75	Air 13 min.	"	32.84	Violet
22a	"	3.0	60	Air 10 min.	"	32.84	"
22c	"	3.0	70	O_2 4 min.	34.22	34.26	"
22d	"	3.0	150	O_2 13 min.	"	34.24	Deep violet

15

Vanadium

Since iron ores may contain from 0.01 to 0.10 per cent. of vanadium, it is necessary to consider the effect of the hydrogen reductor on this element. While it may be permissible in technical ore analyses to neglect such small amounts of vanadium, from the view-point of the precise analyst, however, it is desirable to ascertain definitely the extent of the reduction undergone by vanadium.

Experiments with the reductor on vanadic acid solutions showed variable reduction, depending on acidity, temperature, and concentration of vanadate ion. From many and various experiments, it was concluded that:

(1) complete reduction to tervalent vanadium cannot be attained with the vanadate solutions ordinarily encountered in analytical work;

(2) solutions just acid, at 20° lead to reduction to tetravalent vanadium but if heated tend to go to tervalent vanadium;

(3) solutions with 0.5 to 1.0 M sulfuric acid lead to reduction to tetravalent vanadium whether at 20° or higher temperatures;

(4) long-continued reduction at any temperature and even in 6 M sulfuric acid leads to reduction to a lower stage than tetravalence.

Solutions were now made up to contain 0.1 g. of iron, 0 to 0.003 g. of titanium and 0.002 g. of vanadium, representing the relative amounts of iron and titanium ordinarily encountered in iron ores, but with a vanadium-iron ratio twenty times that usually met with. A method worked out for such mixtures should surely meet the situation likely to occur in analytical practice.

Since the hydrogen reductor method gives the total content of iron plus vanadium, a separate procedure is necessary to determine the correction for vanadium. For this purpose, the method of Campagne[10] was selected as the one best "dovetailing" with the proposed procedure for dissolving the ore. Accordingly, to the hot "synthetic ore" solution, about 20 c.c. in volume, was added potassium permanganate solution in ex-

16

cess, and the pink color destroyed by boiling. Then 30 c.c. of concentrated hydrochloric acid (13 M) were added, and the solution evaporated to a syrup; 10 c.c. of sulfuric acid (9M) were now added, the solution taken down to dense fumes of sulfur trioxide, cooled, diluted with 50 c.c. of water and again taken down to dense fumes. Two evaporations are necessary to ensure the formation of tetravalent vanadium, since hydrochloric acid reduces vanadate to a mixture of tetravalent and tervalent vanadium.[11] After the second fuming, the residue was cooled, treated with 50 c.c. of water, heated till solution was effected, diluted to 150 to 170 c.c., cooled to 20° and titrated with 0.013 M permanganate. This titration gave the vanadium content plus a small color "blank." The titrated solution was then reduced with hydrogen at 20° until colorless, heated to about 90° for fifteen minutes to ensure complete reduction of ferric ion, then cooled rapidly (fifteen minutes) to 20°; at this point the reductor was removed and the solution titrated with 0.013 M permanganate. In a few cases, in order to remove any titanous ion that may have been formed, air was passed into the cool solution for from 5 to 10 minutes before the titration was made. This second titration gave the iron and vanadium content plus the same color "blank" as above; the difference between the two titrations gave the iron content. A "blank" containing everything but vanadium was carried along with the ore solutions and titrated to get the color "blank" to be applied to all the vanadium titers. It is essential to fume strongly to ensure complete removal of hydrochloric acid, otherwise the "blank" varies from 0.10 to 0.20 c.c. of 0.013 M permanganate, 0.10 c.c. being the usual value found.

In Table V are listed the results of the above procedure with "synthetic ore" solutions. It may be noted that the Campagne method occasionally yields high values for vanadium, which causes correspondingly low values for iron. In the aggregate, however, the amount of vanadium found concurs well with that taken; while the iron content as found by the hydrogen reductor checks that found by the zinc reductor within 1.5 parts per thousand.

17

TABLE V.

No.	Ti content Grams	V taken Grams	V found C Grams	Theoretical Fe titer c.c.	Fe titer H c.c.
1	none	.0018	.0020	26.71	26.49
2	"	"	"	"	26.62
3	"	"	.0019	"	26.57
4	"	"	.0015	"	26.65
5	.0032	"	.0017		....
6	"	"	.0021	"	26.69
7	"	"	.0020	"	26.78[1]
8	"	"	.0019	"	26.67
9	"	"	.0021		....
10	"	"	.0018		....
11	"	"	.0019		....
12	none	"	....	"	26.61
13	"	"	....	"	26.80
14	.0032	"	.0016		....
15	"	"	.0017	26.72	26.83[1]
16	"	"	.0016	"	26.67[2]

Note 1: Air for 5 minutes to reoxidise titanous ion.
Note 2: Air for 10 minutes to reoxidise titanous ion.

Theoretical Fe titer is result of three determinations by Zn reductor.
Average of 14 determinations of V by Campagne method = .0018 ± .00017 g.
Average of 11 determinations by H reductor = 26.67 ± .07 c.c.
Corresponds in an average ore to 53.34% Fe ± .14% as against 53.42 by Zn R.

The above conditions for the reduction with hydrogen were necessitated by the fact that long-continued heating leads to the formation of tervalent vanadium. It has been shown that, under the conditions prescribed above, the uncertainty attending the reduction of vanadate ion has no great effect on the determination of iron, even though the vanadium-iron ratio be twenty times that ordinarily encountered in iron ores. With a view to making the method more elastic, without sacrificing safety, it was decided to reduce the ferric ion and vanadate ion in the hot solution, then to reoxidize to tetravalence any tervalent vanadium that may be formed and to titrate ferrous ion plus tetravalent vanadium as above.

Contrary to the widely prevalent idea that ferrous salts in acid solution are easily oxidized by air, it has been found

that bubbling air into hot solutions of ferrous sulfate has little oxidizing effect on ferrous ion. Baskerville and Stevenson[12] found that the passage of air for three hours or more into ferrous sulfate solutions at room temperatures has no appreciable effect on ferrous ion, while at temperatures slightly below the boiling point of the solution, the amount of oxidation was only 2 per cent. in acid solutions and 5 per cent. in neutral solutions. Table VI shows some results obtained with solutions containing 0.06 g. of ferrous iron in a volume of 140 c.c. of 0.7 M sulfuric acid; the aerated solutions were cooled to room temperature before titration. These results, together with those in Table VII are considered sufficient to disprove the prevailing notion.

TABLE VI.

No.	Time for Oxidation Min.	Temp. during Oxidation	Fe titer c.c.
1	none	....	18.32
2	15	$26° \rightarrow 22°$	18.35
3	15	$90° \rightarrow 48°$	18.33
4	30	$100° \rightarrow 36°$	18.40

Regarding vanadium, it has been found that air bubbled through a hot solution oxidizes tervalent vanadium to tetravalence but has no further effect, tetravalent vanadium being stable toward atmospheric oxidation even in hot 18 M sulfuric acid solutions.

Therefore air passed into a hot acid solution containing ferrous ion and tervalent vanadium should convert the latter to tetravalent vanadium but have no effect on ferrous ion. Accordingly, solutions containing 0.1 g. of iron and 0.0018 g. of vanadium in 140 c.c. of 0.7 M sulfuric acid were reduced hot until colorless, whereupon the reductor was removed, the solution heated to boiling and air passed rapidly into the solution for varying periods of time, the temperature being allowed to fall during the reoxidation. Table VII shows the results obtained in experiments with varying reduction periods, varying reoxidation periods and varying titration conditions. The average deviation, disregarding the varying conditions of reduction, reoxidation and titration, is about 2.5 parts per thou-

19

sand, while the average deviation is much less for those experiments where conditions were practically the same. The general average checks the value obtained with the zinc reductor within two parts per thousand. This procedure, then, has been adopted as the one best calculated to give the iron and vanadium content of the ore, the vanadium correction to be determined by the Campagne method as described above.

TABLE VII.

No.	Time for Reduction Min.	Time for Oxidation Min.	Temp. during Oxidation	titer c.c.	Corrected for V c.c.
17	70	17	$100° \rightarrow 50°$	29.43	28.85
19	135	20	$100° \rightarrow 46°$	29.44	28.86
17a	65	15	$83° \rightarrow 52°$	29.42	28.84
20	60	15	$100° \rightarrow 54°$	29.41	28.83
21	95	20	$100° \rightarrow 47°$	29.54	28.96
22	120	20	$100° \rightarrow 51°$	29.49	28.91
24	90	60	$100° \rightarrow 31°$	29.53	28.95
26	115	5	$100° \rightarrow 70°$	29.53	28.95
27	95	5	$100° \rightarrow 72°$	29.59[1]	29.01
28	60	5	$74° \rightarrow 57°$	29.54[2]	28.96
29	70	6	$66° \rightarrow 51°$	29.69[2]	29.11
30	155	5	$100° \rightarrow 70°$	29.69[2]	29.11

| | | | | | 28.95[3] |

Note 1: Titrated hot (40°—50°), adding H_3PO_4.
Note 2: Titrated hot (40°—50°), no H_3PO_4.
Note 3: Average of 12 determinations with an average deviation of .07 c.c.; mean of two determinations by Zn reductor is 29.00 c.c.
Unless otherwise specified the reduced solutions were titrated at 20° to a pink color permanent for at least 1 minute.

The following Table VIII shows the results obtained with iron ores containing no titanium or vanadium and with a Bureau of Standards Sample No. 29, containing 0.594% Ti and 0.054% V. In the procedure used, no attempt was made to eliminate titanium by reoxidation, nor to correct for vanadium.

TABLE VIII.

Iron Ores

No.	Temp.	Time Min.	H_2SO_4 Molar	Zn R c.c.	H. R. c.c.	Remarks
1	20°	80	.7	33.42[1]		
				33.32	33.38	
2	hot, cool	75	.7	32.31		
				32.25	32.36	
3a	" "	105	1.4	62.36[2]	62.40	
3a'	" "	120	1.2	"	62.23	Repetition of 3a
3b	" "	120	1.2	62.47	62.55	
3b'	" "	135	1.4	"	62.49	Repetition of 3b
12a	" "	75	1.7	29.92	30.01	
12b	" "	105	1.8	29.81	29.85	
12c	" "	90	.7	29.91	29.84	
12c'	" "	75	.7	"	29.85	Repetition of 12c
12d	" "	80	.7	29.89	29.91	
12d'	" "	75	.7	"	29.83	Repetition of 12d
12e	" "	100	.7	29.96	29.94	
12e'	" "	75	.7	"	29.86	Repetition of 12e
12f	" "	80	.7	30.10	30.05	
12f'	" "	90	.7	"	29.90	Repetition of 12f
29a	" "	80	1.5	32.34[3]	32.37	B of S Sample Ore 29
29a'	" "	80	1.2	"	32.35	Repetition of 29a

Note 1: $KMnO_4$ Solution D, 1 c.c. = .00344 g. Fe.
Note 2: $KMnO_4$ Solution E, 1 c.c. = .003465 g. Fe.
Note 3: Theoretical value calculated from Bureau of Standards certified average, corrected for Ti and V (55.75% Fe). A certified value uncorrected for Ti and V (55.83% Fe) corresponds to 32.39 c.c.

Procedure Recommended for Iron Ores

Dissolve a 0.2-0.3 g. sample in concentrated hydrochloric acid (13M). Fuse the residue, if any, with potassium pyrosulfate, dissolve in hydrochloric acid and filter into the main solution. If no such fusion is made, add 5 c.c. of sulfuric acid (18M). (If vanadium is present, evaporate to about 50 c.c., then add to the hot solution, permanganate solution until a permanent red color is produced, and boil down to a volume of 30 c.c. Add sufficient hydrochloric acid (13M) to reduce any manganese dioxide or permanganate, then an excess of 10-30 c.c. depending on the vanadium content.) Evaporate to

dense fumes of sulfur trioxide. Cool, add 50-60 c.c. of water and heat until solution is effected. Again evaporate to fumes of sulfur trioxide, cool, and take up in water. Dilute to the volume desired in the hydrogen reduction process, and, if vanadium is present, titrate to the desired color point with 0.013-0.020 M permanganate solution. The selected color should persist for at least one minute. Deduct from this titer the color "blank" and calculate the vanadium content of the ore. The uncorrected titer is to be deducted from the second titer obtained in the following procedure:

Reduce the titrated solution with the hydrogen reductor with a volume of about 150 c.c., and an acidity of about 0.5 M sulfuric acid until it has become colorless while hot; then cool rapidly. When the solution is again at 20°, remove the reductor, washing with water. If vanadium or titanium is present, pass air into the hot solution for at least five minutes. Titrate with the same permanganate solution used above and deduct the first uncorrected titer; the result will give the iron value of the ore. This method is suitable for the determination of iron in ores containing any amount of titanium and as much as 1 per cent. of vanadium.

Determination of Vanadium in Steels, etc.

In steels, vanadium usually occurs in amounts from 0.1 to 0.2 per cent. in the "vanadium" and "chrome-vanadium" steels, and about 2.25 per cent. in certain "chrome-tungsten-vanadium" steels. Accordingly dichromate-vanadate solutions were made up to represent these two types of steels, containing about 0.02 g. of chromium with 0.002 g. and 0.009 g. of vanadium respectively. Since the determination of chromium by ferrous sulfate-permanganate titration has been well established, the hydrogen reduction process was applied only to the determination of the vanadium. It is possible to use the same solution in which the chromium was determined, to reduce the ferric ion and vanadate ion to ferrous ion and tetravalent vanadium, titrate with permanganate, and deduct the permanganate titer equivalent to the total iron added in reducing the dichromate. It is, however, not advisable since it would involve deducting, for example, 20.0 c.c. from a total of 20.5 c.c.

22

to get the vanadium titer of 0.5 c.c. of 0.013 M permanganate. Therefore a separate aliquot of the total chromate-vanadate solution must be used.

Dichromate solutions at 20° were not appreciably reduced by hydrogen. If hot and fairly concentrated however, they were reduced rapidly and definitely to chromic ion. But under these conditions, as with iron-vanadium solutions, it was found impossible to prevent vanadate ion from being reduced to a mixture of tervalent and tetravalent vanadium. Since rapid reduction of dichromate ion and definite reduction of vanadate ion to tetravalent vanadium were simultaneously unattainable, it was decided to achieve the former object in the reduction process, then to reoxidize any tervalent vanadium that may be formed by aerating, as previously done with the iron-vanadium solutions. Consequently, as before, the undesirable reduction product was removed simply by bubbling a rapid stream of clean air into the solution. For this reoxidation the reduced solutions were heated to boiling (100°), and allowed to cool in the air current to about 50°; after 15 minutes of aerating, the solutions were cooled rapidly to 20° and titrated with 0.013 M permanganate solution.

The reduction procedure was varied as may be seen in Table IX, but in all cases where air was used, the amount of vanadium found was in satisfactory agreement with that taken. The lettered numbers refer to solutions of chromic ion and vanadate ion produced by titration of the solution used in the experiment with the corresponding number unlettered. For these solutions, conditions may be varied more widely since there is only vanadate to be reduced; these solutions represent steels or ferrovanadium containing no chromium, and from 0.2 to 2 per cent. vanadium.

The reduction of dichromate ion to chromic ion was usually completed, as indicated by the disappearance of the orange color, in from 30 to 40 minutes. Most reductions were continued for some time, to ensure the reduction of vanadate ion, but the larger reduction period requires a longer time for the reoxidation of tervalent vanadium. From Experiments No. 32 and No. 34, it may be seen that when complete conversion of dichromate to chromic ion has been effected, the vana-

23

date ion has also been reduced sufficiently. By comparing the total time required for reduction and reoxidation of Experiments 30 and 32, it is evident that the procedure in Experiment 32 decreases the time required for the whole process by 0.5 hour.

TABLE IX.

No.	H$_2$SO$_4$ Molar	Vol. c.c.	Temp.	Time Min.	Oxidation Time Min.	V taken Grams	V found Grams	Dev. Grams
24	.7	130	hot, cool	60	15	.0018	.0016	—.0002
25	.7	130	" "	60	20	"	.0019	+.0001
24a	.53	170	" "	30	none	"	.0026	
25a	.53	170	" "	30	17	"	.0017	—.0001
31	.64	140	hot	60	18	"	.0018	....
26	.6	150	hot	60	17	.0089	.0092	+.0003
27	1.4	130	hot, cool	60	15	"	.0089	....
30	.6	140	" "	60	30	"	.0090	+.0001
32	.6	140	" "	40	17	"	.0089	....
33	.6	140	" "	60	15	"	.0091	+.0002
34	.6	140	" "	40	16	"	.0089	....
26a	.5	180	cool	60	15	"	.0089	....
27a	.53	170	cool	45	16	"	.0088	—.0001
28a	.53	170	hot	45	15	"	.0092	+.0003
30a	.5	180	"	30	16	"	.0088	—.0001
26b	.5	360	"	45	17	"	.0086	—.0003
27b	.5	360	"	60	15	"	.0090	+.0001
28b	.5	360	"	30	none	"	.0089	....
29b	.5	360	"	30	17	"	.0085	—.0004

Note: Average deviation is .00013 g. vanadium.

Procedure Recommended for Steels

Dissolve a 2 g. sample (for vanadium content of 2%, use 1 g.) in 1 M sulfuric acid. Dilute with water, heat to boiling, add a saturated solution of sodium bicarbonate until a slight permanent precipitate is formed, then 5 c.c. in excess. Boil for a minute, then filter rapidly. (The filtrate may be used for the determination of manganese; to recover the manganese occluded by the precipitate, dissolve it in dilute sulfuric acid, add sodium bisulfite solution (saturated) to reduce ferric ion, boil off the excess sulfur dioxide, dilute with hot water and reprecipitate the oxides of chromium and vanadium as before;

add the filtrate to that obtained above.) Dry and ignite the precipitate in an iron crucible. Thoroughly mix with it about 10 g. of sodium peroxide and fuse cautiously. When cool, leach with water. Boil the solution for a few minutes to decompose any excess peroxide; cool, then transfer to a 250 c.c. volumetric flask both solution and ferric oxide precipitate. Filter through a dry paper, rejecting the first few cubic centimeters of the filtrate. From the filtrate, withdraw 100 c.c. for the determination of chromium and an equal portion for the vanadium determination.

Determine chromium by the ferrous sulfate-permanganate method.[1] In spite of the color due to chromic ion, the end point in this titration is entirely satisfactory, the violet tinge due to the mixture of pink permanganate with green chromic ion being perfectly reproduceable; a "blank" for the selected color point should of course be made. Here, as in all titrations where tetravalent vanadium is being oxidized to vanadate ion, the color tends to fade; the color point selected as the end point should persist for at least one minute.

For vanadium, dilute the second aliquot to 130-140 c.c., add an excess of 5 c.c. of sulfuric acid (18 M) and reduce hot with the hydrogen reductor. As soon as the color indicates complete reduction of dichromate ion, remove and wash the reductor, heat the solution to boiling and bubble air into it for at least 15 minutes. Then cool to 20° and titrate with 0.002 M permanganate solution.

If the steel contains tungsten, dissolve it in nitric and hydrochloric acids and remove the tungsten as tungstic acid with or without the addition of cinchonine hydrochloride. Occasionally this precipitate occludes chromium; therefore dissolve it in ammonium hydroxide and re-precipitate with hydrochloric acid. Concentrate the filtrates, reduce the solution with bisulfite solution (saturated) and precipitate the oxides of chromium and vanadium with sodium bicarbonate solution; continue as described above.

Sulfuric-phosphoric acid solutions of sodium tungstate were reduced at 80°-90° with the hydrogen reductor. Al-

---

[1] Details may be found in W. Scott's Standard Methods of Chemical Analysis.

though precautions were observed to prevent reoxidation by the air, the extent of reduction in at least a dozen experiments, was found to be never more than 10 per cent. of the theoretical amount for tungsten pentoxide.

Molybdic acid solutions were found to be reduceable by the hydrogen reductor but the extent of the reduction has not been ascertained.

SUMMARY

1. A reductor has been devised to permit the use of the simplest of reducing agents, hydrogen, in quantitative analytical procedures.

2. The effect of this reduction process has been ascertained for ferric ion, titanic ion, vanadate ion, and tungstate ion.

3. A procedure has been worked out which permits of the determination of iron in ores containing as much as 40 per cent. titanium and 1 per cent. vanadium.

4. A method has been evolved for the determination, in the presence of chromium, of vanadium in steels containing 4 per cent. chromium and from 0.2 to 2.25 per cent. vanadium.

5. The effect of the hydrogen reductor upon molybdic acid solutions has been observed but not definitely determined.

BIBLIOGRAPHY

[1] Lundell and Knowles, J. A. C. S., **43,** 1560 (1921).

[2] Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, Bul. **700,** p. 186.

[3] Wardlaw and Clews, J. C. S., **117** (T), 1093 (1920).

[4] Marchetti, Zeit. anorg. Chem., **10,** 66 (1895).

[5] Denham, Zeit. phys. Chem., **72,** 641 (1910).

[6] Teletow, Zeit. f. Electrochem., **12,** 581 (1906)

[7] Diethelm, Zeit. phys. Chem., **62,** 128 (1908).

[8] Eggert, Zeit. f. Electrochem., **20,** 370 (1914).

[9] Eggert, loc. cit.

[10] Campagne, Ber., **36,** 3164 (1903).

[11] Treadwell-Hall, Quantitative Analysis, Fifth Edition, p. **665** (1919).

[12] Baskerville and Stevenson, J. A. C. S., **33,** 1104 (1911).

VITA

James M. Hendel was born in Reading, Pennsylvania, January 24, 1893. He was graduated from the high school of that city in 1909, and from the Phillips Exeter Academy in 1910. In 1914 he was graduated from Princeton University with the degree of Litt.B. From February, 1916, to June, 1917, he pursued courses in chemistry, physics, and mathematics as a "special" student in Columbia College. In the summer session of 1917 he began, and in February, 1919, resumed his graduate work in Columbia University. In the summer session of 1920 he acted as Assistant in Chemistry. From October, 1921, to the present he has been Instructor in the Department of Chemistry of Hunter College of the City of New York.